A Study of the Proposed Two Phase Model for High-Volatile Bituminous Coals

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Introduction

It has been proposed that coal is composed of macromolecular networks and relatively small molecules occluded in macromolecular networks.[1,2] This idea is known as a so-called two phase or host-guest model, which states that a mobile (molecular) phase or a "guest" of relatively low molecular weight such as a pentacyclic triterpane and various long chain alkyl aromatics is physically held inside an immobile (macromolecular) phase or a host of relatively high molecular weight. This is alternatively interpreted as a modified model in which some portions of the mobile phase are bonded to the immobile phase, however, it is thought that a substantial portion of the mobile phase is clathrated within the immobile phase.[3,4]

Although low-molecular-weight (extractable) compounds with difficulty in extraction were investigated in 1960 to early 1970[5,6] they were reestimated in late 1970 to early 1980 as components with mobile protons since the ^1H NMR free-induction decay was applied for coal to distinguish between mobile protons and immobile protons.[7-13] Many works have been recently reported to characterize the two phase model,[14-20] and there seems to be consensus by them that only some portions of a mobile phase can be extracted using conventional extraction procedures because of restricted orifice sizes of immobile phases or networks. However, there is no direct evidence to prove the two phase model.

In this paper, the two phase model was studied by two sets of experiments. One used a combination of chemical class fractionations of coal extracts and mild pyrolyses of coals and extracts. Another used an n-butylamine treatment[22] of coal followed by two different pyrolyses. The concentrations of n-alkanes, polycyclic aromatics (PAH), and pentacyclics, regarded as representative compounds in the mobile phase, were carefully determined. It is concluded that the two phase model is not applicable for high-volatile bituminous coal. It is also inferred that major constituents of coal are uniformly abundant in both extracts and residues.

Experimental Section

Five different rank coals were obtained from Exxon Research and Engineering Co. (Annandale, NJ). ACS reagent and HPLC grade solvents were used. Palladium on activated carbon (10%) was obtained from Alfa Products (Danvers, MA). Tetrahydrofuran (THF) was distilled before use, but other materials were used without purification.

Illinois No. 6 coal was treated as outlined in Figure 1. The coal (6g) was put into a 300 mL bomb (Parr Instrument Co., Moline, IL) in a removable Pyrex liner. After adding n-butylamine (25 mL), evacuating, and purging with N_2 five times, the bomb was heated to 350°C within 10 min with a Parr bomb heater, held at 350 ± 3°C for 4 h with agitation with a magnetic stirrer.

After treatment, the products were washed out with THF, filtered, and Soxhlet-extracted with THF. One part of the THF extract was hydrotreated following the Mudamburi and Given's procedure.[22,23] A sample (2g) was heated with tetralin (5.6 mL) and H_2 (initial pressure 6.5 MPa) in a tubing bomb heated by immersion in a preheated fluidized bed sand bath for 30 min at 425°C. Another sample (2g) was pyrolyzed in cyclohexane (30 mL) and 3% aqueous H_2O_2 (3 mL) at 350°C for 30 min in a bomb. The sample (0.3g) after H_2O_2 treatment was further refluxed in decalin (50 mL) with Pd (10%) on activated carbon (300 mg) at 190°C for 24 h.

Five different rank coals were put into Pyrex glass flasks under a dry N_2 atmosphere and were heated at 250 ± 1 °C and about 660 mmHg pressure under N_2 flow in a Forma Scientific high-temperature vacuum oven 24 h as shown in Figure 2. Starting and pyrolyzed samples (2 - 3 g) were extracted with 200 mL of THF for 24 h in a Soxhlet apparatus under N_2 atmosphere. These extracts were fractioned into chemical classes by column adsorption chromatography on neutral alumina.[24] The fractionation sheme is summarized in Figure 2. The aliphatic and neutral aromatic fractions were analyzed in this study.

Hewlett-Packard Model 5840A gas chromatograph (GC) equipped with a flame ionization detector was used. Sample injection was made in the splitless mode, and helium carrier gas was set at a linear velocity of 50-60 cm s^{-1}. The fused silica capillary tubing (30 m x 0.25 mm i.d.) coated with SE-54 (film thickness of 0.25 μm) was obtained from SUPELCO, INC. (Bellefonte, PA). Compounds were identified by comparison of sample component retention data with those of pure standards and by gas chromatography/mass spectrometry (GC/MS). Mass spectral data were collected with a Hewlett-Packard 5970 mass spectrometer system operated in the electron-impact mode at 70 eV with the ion source and analyzer temperature held at 250 and 280°C, respectively, with the scan speed set at 300 amu s^{-1}.

Results and Discussion

Given's et al.[22,23,25] reported that the yield of n-alkanes and n-alkyl aromatics released from coals by liquefaction in tetralin at 400-425°C was 6-10 times greater than the yield obtained by Soxhlet extraction. They found it difficult to conceive of such homologous series being released from the macromolecular network by thermal reactions, and inferred that the compounds were clathrated inside the network. It is, however, impossible to distinguish between the disruption of chemical bonds and physical bonds using their data. Since most of the organic matter of high-volatile bituminous coals could be extracted with THF after mildly heating in n-butylamine, n-alkanes and PAH were analyzed for the THF extracts from an original and n-butylamine heated coals to investigate physically trapped low-molecular-weight compounds. The THF extract from the n-butylamine heated coal was pyrolyzed using the Given's procedure as well as another different method to differentiate between breaking covalent bond and physical forces (Figure 1). Although the detailed solvation mechanism in n-butylamine is not clear, the differences of abundances of such compounds between Sample II and Sample III or IV are unequivocally due to degradation of chemical bonds. (See Figure 1)

The yield of Sample II from the Illinois No. 6 coal was approximately 85 wt %, which was normalized for the extract and the non-extract because of 18 wt % of the weight gain after heating in n-butylamine. Relative abundances of n-alkanes in the Samples were semi-quantitatively analyzed by GC. The results are shown in Table I relative to n-$C_{20}H_{42}$ in Sample I. It is obvious that the yields of these compounds in Samples III and IV are greater than 10 times of those in Samples I and II, while the yields of these compounds in Samples I and II are almost comparable. From this result, it can be concluded that the increased compounds in Samples III and IV were mostly derived from the thermal pyrolysis of macromolecules, and were not released from clathrated compounds inside the network or immobile phase.

Figure 3 shows the gas chromatograms of the aliphatic fractions of Samples I, II, and IV. It is obvious that n-alkanes with carbon numbers 17 to 22 were relatively increased from Samples II to IV by the pyrolysis. Pentacyclic triterpanes are presumably thermally labile compared with n-alkanes, and their abundances decreased in the order of Samples I, II, and IV as expected. The relative abundances of the major PAH in Samples I - V are also shown in Table I relative to phenanthrene in Sample I. These compounds in Samples III - V were noticeably increased by thermal reactions similar to the n-alkanes. They are apparently important partial constituents of coal macromolecules, or derived from macromolecules during pyrolysis.

It can be interpreted that the great increase of n-alkanes in the product obtained by Given et al. was due to the degradation of coal macromolecules, because more than 10 times of n-alkanes originally present in Illinois No. 6 coal extracts were formed from n-butylamine extracts under their reaction conditions. It is proposed that n-alkyl groups are one of important constituents of Illinois No. 6 coal macromolecules, and most of the n-alkanes in coal-derived products were formed from high molecular weight compounds.

The Illinois No.6 THF extract and a dried mixture of fractions A-3 and A-4 were heated at 250 °C for 24 h and fractionated into chemical classes as shown in Figure 2. Since high-molecular-weight aromatic Compounds strongly adsorb on neutral alumina, they are not eluted by benzene but are found in the A-3 and A-4 fractions.[26] Figure 4 shows gas chromatograms of the A-2 (aromatics) fractions of these heat-treated samples as well as the A-2 fraction of the original coal extract. Significant amounts of material were found in fractions A-1 and A-2 after heating the extract fractions A-3 and A-4 to 250 °C for 24 h. Simply refractionation a mixture of A-3 and A-4 gave very little material in the A-1 and A-2 fractions, so it is clear that the origin of the new compounds is pyrolysis. Furthermore, many new peaks are found in the chromatograms of these fractions. Clearly new compounds are present. Their origin could only be pyrolysis reactions occurring in a coal extract at 250 °C. Among the new compounds are a number of low-molecular-weight aromatic compounds such as alkylbenzenes, alkylnaphthalenes, phenanthrene, and alkylhydroaromatic triterpanes, presumably formed by pyrolysis of the high-molecular-weight fractions. Both results, obtained by different experimental procedures, are clearly consistent.

There were two purposes for the reaction leading to Sample V. One was to confirm the identification of the hydroaromatics, because it is known most of the hydroaromatics are dehydrogenated by Pd on activated carbon at the low temperature used in this study. The second was to investigate the effect of aromatization by dehydrogenation during coal liquefaction.

Hydroaromatics such as hydroanthracenes, hydrophenanthrenes, and hydropyrenes were abundant in Sample IV compared to Sample III, while 4- and 5- ring PAH such as chrysene and benzopyrenes were abundant in Sample III (Table I). It is thought that the major reaction producing Sample IV from Sample II is a mild radical cracking while the major reaction involved in forming IV from Sample II is hydrocracking including thermal aromatizations at high temperature. Hydroaromatics, therefore, seem to be one of important constituents of coal macromolecules. Although aryl groups such as biphenyls and phenylnaphthalenes are abundant in Samples III and IV, carbon linked aromatics were not found in these samples at a significant level. The abundances of the aliphatics and aromatics in Sample V are quite similar to other coal liquids such as the Solvent-Refined Coal II heavy distillate (SRC II HD),[27] although the feedstock was a different coal.

From above results, we can infer as the follows: coal components are quite uniform despite extracts or non-extracts. Most *n*-alkanes and PAH are not physically trapped inside networks. They are both free molecules and partial constituents of macromolecules or derived from macromolecules during pyrolysis, and can be thought as "preferred" constituents.[27] Most the neutral free low-molecular-weight compounds can be extracted under conventional conditions, such as a Soxhlet extraction.

Since the two phase model does not appear to be appropriate for Illinois No. 6 coal, the coal should be considered as a mono phase. Coal molecules contain "preferred" components such as *n*-alkanes and PAH studied in this paper. The preferred components are estimated for Illinois No. 6 coal. It also seems that aromatics linked with a couple of carbons are not so substantial in Illinois No. 6 coal as above "preferred" structures.

The mono phase model and its "preferred" structures contained in the Illinois No. 6 coal are essentially different from the two phase model. The "preferred" moieties are partial constituents of coal macromolecules regardless of molecular weight, and some exist as free molecules of low-molecular-weight.

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Table I. Approximate Relative Abundances of Selected Compounds in Each Sample

	Sample[b] I	II	III	IV	V
$\underline{n}$-$C_{17}H_{36}$	1	4	40	110	40
$\underline{n}$-$C_{18}H_{38}$	2	5	40	70	70
$\underline{n}$-$C_{19}H_{40}$	2	4	50	30	30
$\underline{n}$-$C_{20}H_{42}$	1	3	40	20	20
$\underline{n}$-$C_{21}h_{44}$	2	6	80	20	20
$\underline{n}$-$C_{22}H_{42}$	0.3	0.5	30	10	10
naphthalene	a	a	3	4	10
fluorene	a	a	0.2	5	5
phenanthrene	1	1	3	10	20
anthracene	0.05	0.05	0.1	1	4
fluoranthene	a	a	2	4	5
pyrene	0.1	0.1	2	3	4
benzo[<u>b</u>]fluorene	a	a	0.4	0.5	0.05
benz[<u>a</u>]anthracene	a	a	2	0.03	0.06
chrysene	a	a	2	0.1	0.01

[a] <0.01
[b] Relative abundances are shown as $\underline{n}$-$C_{20}H_{42}$=1 for aliphatics and phenanthrene=1 for aromatics.

Table II. Neutral Aromatics Identified in Original and Pyrolyzed Illinois No. 6 Samples

Peak No.	Molecular Mass and/or Major Fragments[a] m/z	Possible Structure
1	106, 120	C_2- and C_3-benzene
2	142	2-methylnaphthalene
3	142	1-methylnaphthalene
4	156	C_2-naphthalene
5	168	methylbiphenyl
6	182	C_2-biphenyl
7	355(100), 281(62.5), 221(44.5), 207(77.0)	unknown
8	180	methylfluorene
9	178	phenanthrene
10	178	anthracene
11	194	C_2-fluorene
12	198	methyldibenzothiophene
13	355(3.3), 281(5.3), 223(10.3), 207(22.1), 149(100)	unknown
14	192	methylphenanthrene
15	208	C_3-fluorene
16	202	pyrene
17	216	methylpyrene
18	228	benzo[a]anthracene
19	281(2.0), 259(3.3), 241(1.2), 207(8.7), 147(14.6), 129(100)	unknown
20	228	chrysene
21	279(9.5), 207(37.8), 167(30.1), 149(100)	unknown
22	412(12.0), 397(10.4), 384(6.1), 369(4.0), 281(21.9), 207(100)	alkyl pentacyclic hydroaromatics
23	440(2.0), 339(28.3), 281(22.1), 207(100)	alkyl pentacyclic hydroaromatics
24	429(3.4), 415(3.4), 289(30.6), 281(20.5), 207(100)	unknown

[a]Numbers in parentheses denote relative abundances of mass spectra.

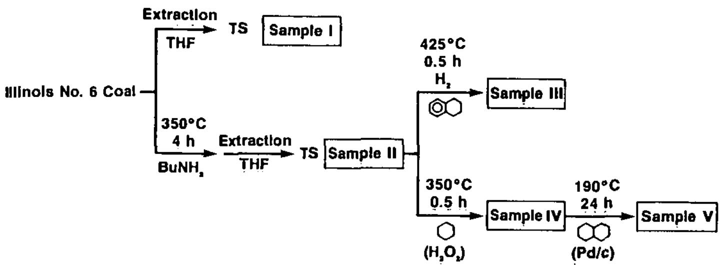

Figure 1. Solvent treatment and reaction scheme of Illinois No. 6 coal.

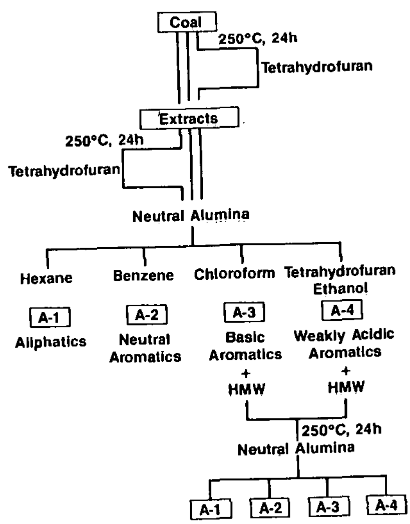

Figure 2. Fractionation and pyrolysis scheme. Key: HMW = high-molecular-weight compounds.

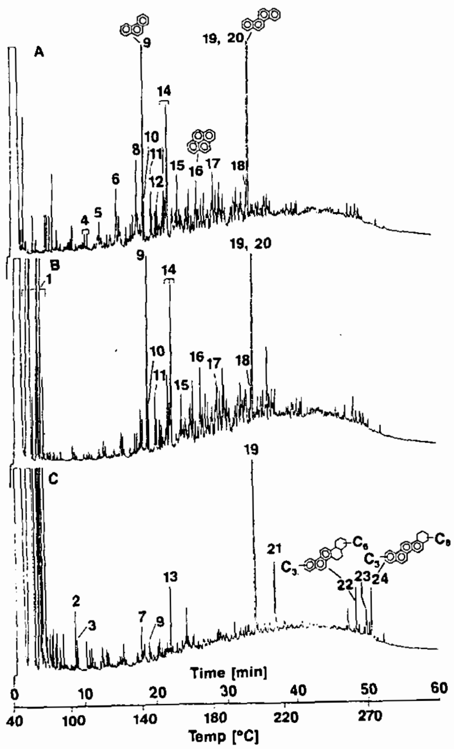

Figure 3. Gas chromatograms of aliphatic fractions of (A) Sample I, (B) Sample II, and (C) Sample IV.

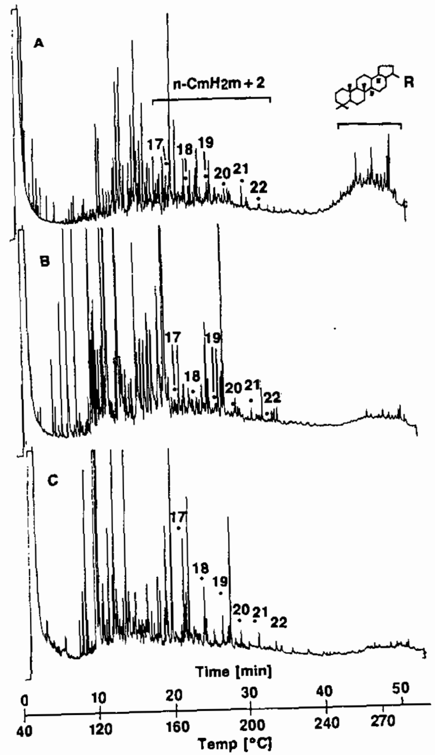

Figure 4. Gas chromatograms of the aromatic fractions (A-2) of the (A) original coal THF extract, (B) heat-treated THF extract, and (C) heat-treated A-3 and A-4 mixture for Illinois No. 6.